INTERMEDIATE TEMPERATURE POLYMER ELECTROLYTE INCORPORATED WITH POLYOXOMETALATES FOR FUEL CELL APPLICATIONS

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ABSTRACT

We report here some results of proton conducting inorganic/organic hybrid polymer membrane materials that were synthesized by sol-gel process using organically modified alkoxysilane precursor with polyoxometalates of different structures. Polyoxometalates $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_6P_2W_{18}O_{62}$ were chosen for the study. The proton conductivity of the membrane made with the above polyoxometalates increased with the increase of the temperature in the presence of saturated water vapor, measured with a four-electrode configuration, and at 100°C the conductivity of the membranes is found to be in the range of 10^{-3} O^{-1} cm^{-1}. Thermal analysis of the membranes showed that the membrane materials have different weight loss profile with structurally different polyoxometalates being incorporated.

1. INTRODUCTION

Development of polymer electrolyte membrane materials in order to work at intermediate temperatures (80~140°C) for hydrogen and direct methanol fuel cells is needed for the benefits of the reduced purity requirements for fuel, the potential to use non-noble metal catalysts instead of expensive platinum, and the improved overall fuel cell performance that is due to the enhanced electrochemical reaction kinetics. In addition, higher operating temperature above 80°C may improve the potential of water and heat management. Recent literatures (Kim et al., 2003; Honma et al., 2003) reported some inorganic/organic hybrid electrolyte membranes made with polyoxometalate to have good proton conductivity at temperatures above 100°C. In this presentation, we summarize the results of our investigation on $H_3PW_{12}O_{40}{\cdot}12H_2O$, $H_4SiW_{12}O_{40}{\cdot}13H_2O$, and $H_6P_2W_{18}O_{62}{\cdot}20H_2O$ polyoxometalate acids that were incorporated in inorganic/organic hybrid poly(tetramethylene oxide) membranes, along with the results of $H_3PW_{12}O_{40}{\cdot}12H_2O$ in poly(ethylene oxide) membranes.

2. EXPERIMENTAL

The inorganic/organic hybrid precursor was synthesized by combining poly(tetramethylene glycol) (MW 650) or poly(ethylene glycol) (MW 400) with 3-(triethoxysilyl)propyl isocyanate under nitrogen at 70°C for 4 days (Honma et al., 1999). The organically modified alkoxysilane precursor in isopropanol and the polyoxometalate acid dissolved in isopropanol was used to make a sol solution. The sol solution was then cast into Teflon lined petri dish, and was allowed the solvent slowly to evaporate over twenty-four hours at room temperature. The resulting membranes were transparent and flexible. The polyoxometalate acids were synthesized according to literature procedures (Bailar, 1939; Contant, 1990; Teze et al., 1990). The $H_6P_2W_{18}O_{62}{\cdot}20H_2O$ acid was prepared by converting K^+ to H^+ with ion-exchange method (Creaser et al., 1993). These acids serve as both the catalyst for the hydrolysis of the sol-gel process and as the proton-conducting contributor of the membrane. The proton concentration was maintained at the molar ratio of 1:3 with respect to the hybrid polymer precursor in all the membranes. The membranes were heated at 120°C for two hours to ensure the completion of polymerization reaction.

AC impedance measurements of the membrane films were conducted in a four electrode impedance measurement apparatus (Cahan et al., 1993) under saturated water. AC impedance data were acquired between 10 Hz and 100 kHz. Thermal gravimetric measurements were carried out from room temperature to 800°C with a heating rate of 5°C/min.

3. RESULTS AND DISCUSSION

3.1 Thermal Stability

TGA profiles of the three polyoxometalate acids from room temperature to 800°C have three weight loss steps. The first and second steps below 300°C are the water released from the crystalline phases of the solid acids. The ionic structures of the polyoxometalates remain intact at this point, and the water loss is reversible. The properties of the polyoxometalate anions can be recovered by adding additional water to the dehydrated solid acids. The third weight loss step is between 300 and 500°C, and it corresponds to the thermal decomposition of the polyoxometalate anionic structure. Based on the temperature of the last weight loss step, we found that $H_3PW_{12}O_{40}{\cdot}12H_2O$ has the highest decomposition temperature at just above 400°C, while $H_4SiW_{12}O_{40}{\cdot}13H_2O$ at slightly below 400°C. The acid $H_6P_2W_{18}O_{62}{\cdot}20H_2O$ showed the thermal decomposition temperature at about 300°C.

For the poly(tetramethylene oxide) membranes that were obtained at room temperature without any heating,

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the TGA results of these membranes revealed basically identical weight loss profile for the acids of $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ that have the same anionic structure. The other acid, $H_6P_2W_{18}O_{62}$, which is structurally different with a larger size than $H_3PW_{12}O_{40}$, has the weight loss of the membrane occurred at slightly higher temperature. This can be interpreted as a delayed component release from the poly(tetramethylene oxide) membrane that has $H_6P_2W_{18}O_{62}$ incorporated. On the other hand, the membranes with $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ have a component release at a lower temperature. These results demonstrate that different anionic structures of the polyoxometalates do make a difference in the formation of inorganic/organic hybrid polymers.

The TGA results for the membranes that were treated at 120°C/2h are in agreement with the findings of (a) the membranes with $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ are almost identical; and (b) the membrane with $H_6P_2W_{18}O_{62}$ has about 60% weight loss that occurs between 200°C and 500°C, while the other two membranes have only about 50% weight loss in the same temperature range. In another word, some components in the membrane of $H_6P_2W_{18}O_{62}$ cannot be released at 120°C, and they can only be released at the temperature above 200°C.

3.2 Proton Conductivity

The proton conductivity measurements were carried out on the 120°C/2h treated poly(tetramethylene oxide) membranes with $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_6P_2W_{18}O_{62}$. An untreated membrane of poly(ethylene oxide) with $H_3PW_{12}O_{40}$ acid was also tested. The data are listed in Table 1. It shows that the membranes made with the acids of the same ionic structure ($H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) basically have the same proton conductivity, which is in good agreement with the results of TGA measurements (they have the same weight loss profile). The membrane with the acid $H_6P_2W_{18}O_{62}$, however, yields slightly higher conductivity at 80°C and 100°C. The difference in polyoxometalate structure may lead to different degree of hydration and the distribution of hydrophilic and hydrophobic phases in the membranes, which is believed to relate to the conductivity. Also noted is the higher conductivity of the poly(ethylene oxide) membrane that was untreated at 120°C. This untreated membrane may be more porous and contain more water than those treated at 120°C for 2 hours.

Table 1. Conductivity (S/cm) of the membranes

	80°C	100°C
PW_{12}^{*}	$7.47x10^{-3}$	$9.32x10^{-3}$
PW_{12}^{**}	$0.63x10^{-3}$	$1.10x10^{-3}$
SiW_{12}^{**}	$0.62x10^{-3}$	$1.06x10^{-3}$
$P_2W_{18}^{**}$	$1.16x10^{-3}$	$1.55x10^{-3}$

* Untreated poly(ethylene oxide) membrane;
** 120°C/2h treated poly(tetramethylene oxide) membranes.

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CONCLUSION

Different anionic structures of the polyoxometalates were found to play a role in the formation of inorganic/organic hybrid polymer membranes and in their thermal property and proton conductivity.